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54 Hydraulic cement mix and process for its production.

57 A hydraulic cement mix comprising a hydraulic cement, aggregate in an amount of up to 80 % by weight based upon the total weight of said cement mix, sufficient water to effect hydraulic setting of the cement, and an air-entraining additive consisting essentially of a coconut fatty acid diethanolamide produced by reacting alkyl ester of coconut acid with diethanolamine, said additive being in an effective amount whereby air will be entrained in said mix in an amount of 3 % to 9 % by volume of said mix.

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Hydraulic cement mix and process for its production

This invention pertains to concrete and cement additive compositions, known as air-entraining admixtures, for incorporation in hydraulic cement mixes such as portland cement concretes and mortars, but not limited thereto, for the purpose of increasing the durability in the hardened state of such mixes, to freeze-thaw cycles under conditions of water saturation. The increased durability of the cementitious mix under such conditions is the result of the development in the plastic portland cement mix of a system of air bubbles that will remain in the mix after hardening and meet the specifications of resistance to freezing and thawing stipulated in ASTM designation C-260. This requires that the air void system be a specified amount as volume percent of the hardened cementitious mass, and that it have bubbles within a specified range of sizes and spacing parameters as designated by ASTM specification C-457. It is well known in the art that in order to meet these requirements, it is necessary to use surface agents or surfactants to obtain the desired amount of air entrainment.

There are a number of chemical agents to achieve the specified air entrainment system. Generally, these are organic chemicals which are broadly classified as soaps and detergents. One of the best known chemical agent of this type is known in the art as Vinsol resin, which is a wood resin salt and is the standard against which other air-entraining agents are tested under ASTM specification No. C-233. Vinsol resin is normally employed as an aqueous alkaline solution that is added to a plastic, cementitious mix, either alone or in combination with other chemical admixtures. In the latter case, the Vinsol resin solution is added separately because of its chemical incompatibility with many other admixtures, due to the fact that the pH and the presence of calcium and various other ions renders insoluble the alkali-neutralized acids comprising Vinsol resin.

It is also known in the prior art to use a variety of surfactants, both anionic and nonionic, in the broad class of detergents to obtain a desirable degree of air entrainment in cement, mortar and concrete. Often these are used in various combinations. Some of these surfactants are sulfated ester ammonium salts of higher primary alcohols (or additional products with ethylene oxide), alkylbenzenesulfonic acid salts, salts of petroleum acids, fatty acids and proteinaceous substances, and organic salts of sulfonated hydrocarbons.

For example, U.S. Patent No. 4,249,948 disclosed the use of an alpha olefin sulfonate with a water reducing agent wherein the former acts as an air-entraining agent in a hydraulic cement composition. U.S. Patent No. 4,046,582 disclosed the use of a higher secondary alcohol oxyalkylene sulfate as an air entraining agent. PCT International Application No. WO 85/01,500 (U.S. Patent Application No. 537,185; filed 9-29-83) discloses the use of a multicomponent air-entraining additive for hydraulic cement mixes which comprises a three-component mixture of an alkylarylsulfonic acid salt, an alkanolamine salt of a fatty acid such as tall oil, and a nonionic component selected from polyethylene glycol derivatives and diethanolamine adducts of cocamid derived from coconut oil.

However, these air-entraining additives are not entirely satisfactory with respect to the stability of the air bubbles in concrete, the ability to perform in the presence of fly ash in the mix, the effect on improving the workability of the concrete, the need to use higher dosages of admixtures known in the art, or tendencies to either lose air or to uncontrollably increase air content, as mixing time is extended. Loss of workability is measured by the slump cone in accordance with the American Society for Testing and Materials (ASTM) designation C-143. The biggest disadvantage is the reduction in compressive strengths by as much as 5 % strength loss per 1 % increase of entrained air. This loss is due, in part, to an irregular bubble sizing and the coalescence of bubbles in the mix causing larger voids, this reducing the compressive strengths.

Thus, there exists the continuing need to discover new and improved air-entraining agents, especially ones that will overcome the problems described above.

The present invention concerns a chemical additive for combining into hydraulic cement mixes, such as portland cement concrete, mortar and grout, including portland cement mixes which contain various amounts of fly ash or slag, for the purpose of entraining air therein, and the resulting improved mixes for incorporating an additive composition.

For purposes of this invention the term "hydraulic cement" refers to all cementitious compositions based primarily on silicates capable of being set and hardened by the action of water, such as portland cements, sulfate-resisting cement, blast furnace cements and pozzolanic cements, including cement mixes where a portion of the portland cement has been replaced by fly ash or slag. The term "portland cement" refers to all cementitious compositions which have a high content of tricalcium silicate, conforming with the specifications set forth in ASTM designation No. C-150, and the portland blended cements such as those described in ASTM designation No. C-595.

Broadly, the invention comprises a portland cement mix including fly ash and/or slag cement, aggregate, sufficient water to effect hydraulic setting of the cement, and an air-entraining additive consisting essentially of an ester-derived coconut acid diethanolamide, also known as cocamide diethanolamine or cocamide DEA, as more fully described hereafter. The cocamide DEA be added in any convenient form, although it is most convenient to add it as an aqueous solution.

The dosage used should be an amount which is effective in entraining the desired amount of air, usually measured as a volume percentage of the hydraulic cement mix. As is known in the art, the amount of air entrained desired and intended to be is usually in the range of 3 % to 9 % air, by volume. This amount of air is achieved by a dosage of ester-derived cocamid DEA of between about 0,001 % and 0,01 % by weight based upon the weight of the cement.

The unexpected and nonobvious result obtained by employing ester-derived cocamide DEA by itself in a cementitious system undergoing extended mixing is to yield with a favorable dosage response an excellent air void system stable in the plastic cementitious system and having a desirable improved size distribution in the cementitious system after hardening, while yealding increased compressive strengths over reference mixes.

It is therefore the object of this invention to provide improved air-entrained portland cement mixes, including concrete, mortar, grout and dry mixes, which include an additive composition that will advantageously entrain an air void system having desired characteristics when said additive is employed over a relatively wide dosage range, or have a superior dosage response relative to functionally similar additives known in the art.

It is another object of this invention to provide improved strength results which include an additive composition that will entrain an air void system and increase compressive strengths over known air-entraining agents.

The term "cocamid DEA" is a name Cosmetic, Toiletory, and Fragrance Association, or CTFA, has applied to a wide variety of coconut acid-based compositions comprizing diethanolamine adducts of cocamides. Although they are all called cocamide DEA, they are produced by a variety of reactions. In one type of reaction, a 1:1 molar ratio reaction is produced between diethanolamine and either a coconut acid, also known as coconut fatty acid; an alkyl ester, usually methyl ester of a coconut acid; or a coconut acid-based triglyceride, such as coconut oil. In another type of reaction, a 2:1 molar ratio is employed in the so-called Kritchevsky process, which is described in U.S. Patent No. 2,094,809 to W. Kritchevsky.

The present invention has resulted from the unexpected discovery that cocamide DEA, produced by the methyl ester process, although other esters could be used, will, when employed by itself in effective amounts in hydraulic cement mixes, produce stable volumes of air having desirable size and distribution, such as are employed to increase the freeze-thaw durability of hydraulic cement mixes or to produce air-entrained hydraulic cement mixes for other reasons. Additionally, it was discovered that higher compressive strengths were beneficially achieved using the additive of the invention. For convenience, cocamide DEA derived by the ester process will be described as ester-derived cocamide DEA.

Ester-derived cocamide DEA is commercially available under the trademarks Comperlan KD and Standamid KD from Henkel International GmbH, Düsseldorf, West-Germany, and Ninol 49CE from Stepan Company, Northfield, Illinois.

The term "coconut acid" usually means a mixture of fatty acids derived from the hydrolysis of coconut oil, and having acid chain lengths varying from 6 to 18 carbons, but mostly 10, 12 and 14 carbons. A preferred coconut acid is one consisting approximately of the following range of fatty acids

Lauric Acid 46-58 %
 Myristic Acid 15-23 %
 Palmitic Acid 8-14 %
 Stearic and Oleic Acid 7-24 %

Further, the coconut acid preferably should have an acid value of between about 246 and 260, a saponification value of between about 247 and 262, and an iodine value of between about 10 and 20.

The resulting cocamide DEA reaction product from the reaction of the coconut ester and diethanolamine will preferably comprise approximately the following composition and have a pH value (of a 1 % solution) in the range of 8-10 and a density in the range of 8,3 to 8,5 pounds per gallon (0,99 to 1,02 kg/l), with preferably about 8,43 pounds per gallon (1,01 kg/l) :

Coconut Amide 85-90 %
 Coconut Ester 0-10 %
 Free Coconut Acid 0-0,5 %
 Free Diethanolamine 0-5 %
 Water 0-0,5 %

In the practice of the present invention the additive is incorporated into hydraulic cement mixes such as portland cement concretes and mortars in amounts sufficient to yield an entrained air void system of the proper amount and quality. As a practical matter the additive is incorporated into the mix as an aqueous solution, which may be of any convenient concentration.

The additive may be incorporated into the mix as a portion of the mix water but it may also be incorporated in any other convenient manner, including adding it to the dry mix or aggregate before the water is incorporated therein.

The term "entrained air" is intended to have the meaning found in the art, namely that by using an agent for that purpose, an intended and desirable amount of air, i.e. 3 % to 9 %, by volume, based upon the total volume of the hydraulic cement mix, will be incorporated into the plastic hydraulic cement mix and ultimately in the hardened concrete. By this means the durability of workability of a plain or non-air-entrained concrete or mortar can be improved. Further, the materials which comprise a concrete mix, and the mixing itself, can introduce some air into the mix, and often, such is referred to as entrapped air. The additive of the present invention is beneficial in that it unexpectedly produced an intended and desirable amount of air entrainment which further proved to be stable during extended mixing and to be beneficial to the hardened concrete because it resulted in increased compressive strengths.

The term "aggregate" is intended to include both coarse aggregate, such as crushed stone or gravel, and fine aggregate, such as sand, as is common in the art. In general, the aggregate in mortars may be sand or other fine aggregate meeting the requirements of ASTM designation No. C-33. The proportion of coarse aggregate and fine aggregate will vary depending upon the properties and use of the concrete or mortar. In most cases, although not limited thereto, the coarse aggregate will be within the broad range of 2 inches (7.6 cm) to 4 mesh, while the size of the fine aggregate will be within the broad range of about +4 mesh to -200 mesh U.S. Standard Sieve (ASTM C-11). The coarse aggregate will usually be of mineral origin, such as gravel or crushed limestone, but it may be a manufactured aggregate, such as a slag. The amount of aggregate can be up to 80 % by weight, based upon the total weight of the hydraulic cement mix, with the range of 20 % to 80 % by weight being preferred.

For both mortars and concretes, the amount of water employed generally would be enough to effect hydraulic setting of cementitious material in the mix and to provide suitable workability in the plastic state. This would broadly range from about 15 % to 30 % by weight of the cementitious materials in mortars and about 50 % to 85 % by weight of the cementitious material in concrete mixes. The precise proportion of water will depend on the end use of the cementitious mix as well as on its composition.

In order to illustrate the effectiveness of ester-derived cocamide DEA in generating air bubbles, as compared to other known and potential air-entraining agents, selected agents were tested in a modified Henkel Foam Test. The following is the "Foam Test Methodology" stated in a Henkel International GmbH technical bulletin for Standamid brand alkanolamides :

"Foam Test Methodology

"The following test procedure; developed by Henkel; is a "simple way to make accurate determination of foam volume and foam "drainage : Prepare a 10 % aqueous solution of product being "evaluated. Add six (6) grams of this solution to 144 grams of "water, hardness 50 ppm, heated to 29°C : 1°C. Agitate for ten "(10) seconds in an osterizer-type blender. Stir/medium speed "agitation. Measure the initial foam volume to the nearest 5 ml, "and then record the position of the foam/water interface after 3,5 "minutes. This later reading represents the foam drainage."

The test was modified by using 5 % by weight aqueous solutions and placing 300 cc of each solution in a measuring container, graduated in millimeters, for use with the osterizer-type blender. As per the Henkel test, the solution is agitated for ten (10) seconds at medium speed. The mixing generates a certain amount of foam which floats above a liquid interface and which is measured as the initial interface. The container is then allowed to stay undisturbed for one (1) hour. When this is done, some or all of the foam returns to liquid. This liquid return is called "foam drainage", and a new liquid-foam interface, or final interface, is established somewhere between the initial interface and the 300 cc level at which the liquid started. The amount of the final liquid-foam interface is then measured. The percent of foam drainage is calculated by dividing the difference between the final and initial interfaces by the difference between the 300 cc level of each solution and the initial interface and multiplying by 100. The results for each tested agent are reported in Table I. The amount of foam drainage is considered to be a reflection on the stability of the bubbles generated.

Also reported in Table I is the unit weight of the bubbles generated, called bubble density. To obtain the unit weight, a further test was done using the same modified Henkel foam test methodology. Three hundred (300) cc of each solution were placed in the osterizer-type blender, agitated for ten (10) seconds at medium speed, and then allowed to sit undisturbed for one (1) hour. The bubbles or foam remaining were then removed from the mixer, placed in a volumetric measuring unit and weighed. The values were then converted to weight per one cubic foot.

TABLE 1

| Agent Tested | Foam Drainage (1%) | Bubble Density kg/m |
|---|--------------------|------------------------|
| Cocamide DEA (Ester-Derived)* | 16,7 | 33,182 |
| Cocamide DEA (Kritchevsky Process-Derived) | 96,6 | 15,070 |
| Cocoamido Propyl Betaine | 99,4 | 2,029 |
| Cocamide DEA (Ester-Derived)** | 86,0 | 18,257 |
| Cocamide DEA (Oil-Derived) | 97,3 | 6,955 |
| Sodium Lauryl Sulfate | 99,3 | 2,174 |
| Ammonium Lauryl Sulfate | 98,0 | 2,463 |
| Lauryl Sulfate Triethanolamine | 99,8 | 1,884 |
| Sodium Octyl Sulfate | 99,2 | 1,304 |
| Disodium Mono-Oleamide/Diglycol Sulfosuccinate | 98,3 | 2,463 |
| Wood Resin Salts | 98,1 | 2,608 |
| Alkyl Phenoxy Polyethoxy Ethanol | 98,0 | 2,753 |
| * Supplied by Source I (Henkel) | | |
| ** Supplied by Source II (Stepan) | | |

These results demonstrate that ester-derived cocamide DEA has a superior combination of bubble volume retention as measured by the low foam drainage and greater unit weight. Of particular interest is the performance against wood resin salts, such as are used in Vinsol resin air-entraining admixtures, as compared to ester-derived cocamid DEA. The ester-derived cocamide DEA from Source I performed the best and resulted in only 16,7 % foam drainage versus 98,1 % for the wood resin salts. The cocamide DEA from Source II was not as good a performer as that from Source I, but still had an acceptable combination of foam drainage (86,0 %) and bubble density (0,161 kg/m³), especially compared, e.g., to the Kritchevsky process-derived cocamide DEA, which had a relatively high bubble density of 0,133 kg/m³, but a very high foam drainage of 96,6 %. Thus, an ester-derived cocamid DEA having a foam drainage of at most about 86 % or less and a bubble density of 0,154 kg/m³ or more is preferred.

The reason for the greater unit weight for ester-derived cocamide DEA is speculated to be due to greater thickness of the bubble walls. When a portion of the bubbles produced in the modified Henkel foam test is placed on a spherical depression slide and examined using a standard laboratory microscope, the cocamide DEA bubbles from Source I are seen as spherical bubbles having thicker walls, while the wood resin bubbles are relatively thinwalled and tend to be less than spherical with some shapes being oblong. This sort of difference should produce a more stable air and uniform bubble structure in a hydraulic cement mix environment.

For the purpose of illustrating the advantageous results obtainable by the practice of the present invention in hydraulic cement mixes, concrete mixes were prepared according to ASTM designation Nos. C-494 and C-233. Mixes containing the additives of the present invention and Vinsol resin additives were made. The sequence of operations in this procedure were : preparation of concrete mixes with a nominal slump of $0,05 \text{ m} \pm 0,012 \text{ m}$ and a dosage of air-entraining admixture per 45,359 kg of cement such as would produce an air content of $5,5 \% \pm 0,5 \%$ by volume of the concrete. Each mix was designed for a total of 214,432 kg/m³ portland cement, a sand-aggregate ratio of 0,89, and the same waterto-cement ratio (0,31). The concrete, with an appropriate amount of water to attain the specified slump value was then mixed in a concrete mixer of 0,17 m³ capacity. Next, 0,152 x 0,304 m cylinder specimens were taken for subsequent determination of compressive strengths and the parameters of the air void system after hardening. The initial air content of a sample of the plastic concrete was determined by the pressure-meter method as described in ASTM standard test method No. C-231 and the slump value, which is an index of workability, was determined in accordance with ASTM standard method No. C-143.

The results of the tests are shown in Table II and a comparison is made between an ester-derived cocamide DEA (from Source I) and Vinsol resin air-entraining agent. In each case the rate of hardening was within the ASTM No. C-233 specification. It can be seen from Table II that the ester-derived cocamide DEA produced the intended and desirable amount of air as well as favorable air retention and further achieved significant compressive strength gains in comparison to the concrete containing Vinsol resin.

TABLE II
TEST RESULTS

| | Vinsol Resin (Control) | Ester-Derived Cocamide DCA | Difference As Percent Of Control |
|-----------------------------|------------------------------|-------------------------------|--|
| Entrained Air (%) | 6,0 | 5,7 | |
| Compressive Strength (M.Pa) | | | |
| 1 Day | 13,44 | 16,27 | 121 % |
| 3 Days | 23,51 | 27,23 | 116 % |
| 7 Days | 28,54 | 38,23 | 109 % |
| 28 Days | 36,09 | 38,88 | 108 % |

In order to evaluate the entrained air in the hardened concrete, one of the specimens from the concrete made using ester-derived cocamide DEA and produced in the tests discussed above was examined microscopically in accordance with ASTM standard method No. C-457, with the results being reported in Table III.

TABLE III
AIR VOID ANALYSIS

| | Air Content | | Paste# | Specific | Spacing |
|---|------------------|-------------------|--------------------|-----------------------|-------------|
| | % by Volume | | Content | Surface | Factor |
| | <u>(Plastic)</u> | <u>(Hardened)</u> | <u>% by Volume</u> | <u>m⁻¹</u> | <u>I, m</u> |
| 5 | 5,7 | 6,7 | 23,83 | 20,000 | 0,000175 |

Sum of the volumes of portland cement and mixing water.

As can be seen, the spacing factor I is 0,000175 m, which is less than the 0,0002 m factor and more than 0,0001 m, which is the usual recommended limits on the spacing factor for durable, i.e., resistant to freezing and thawing, concrete.

In another test, a comparison was made between plain concrete, which was the control and contained no air-entraining agent, a Vincol resin mix and a mix containing an ester-derived cocamide DEA (Source I). The mix designs were similar to those in Table II except that the slumps were 4 inches \pm 1/2 inch. As can be seen in Table IV, the ester-derived cocamide DEA achieved significantly higher compressive strengths than the Vinsol resin and the plain control mix, and produced desirable air entrainment.

TABLE IV
Control Vinsol Resin Ester-Derived
Mix Mix DEA Mix

| | | | | |
|----|---------------------------|-------|---------|---------|
| 25 | Dosage (% by Weight) | - | 0,0087 | 0,0039 |
| | of Cement | | | |
| 30 | Air Content (% by Volume) | - | 5,1 % | 5,8 % |
| | at 1.0 Minutes | | | |
| | 7 Day Avg. MPa | 24,11 | 24,27 | 26,34 |
| 35 | (% Compared to Plain) | | (100,7) | (109,2) |
| | 28 Day Avg. MPa | 30,33 | 29,75 | 32,63 |
| | (% Compared to Plain) | | (98,1) | (107,6) |

In yet another test, extended mixing time was done with a series of concrete mixes containing an ester-derived cocamide DEA from Source I (Mix A), ester-derived cocamide DEA from Source II (Mix B), and a Kritchevsky process-derived cocamide DEA (Mix C), such as used in the tests reported in Table I. This test was done to establish the performance of stability of the air bubbles over a period of mixing time such as would be comparable to concrete mixed in the field. The mix design is shown in Table V. The mixing was done continuously for 50 minutes, except when samples were taken to measure the air content. At the time additional water was added to restore the slump, as close as possible to its original value.

TABLE V
Concrete Mix Design

| | | | |
|----|------------------------------|------------------------------|--------------------|
| 5 | Cement | 256 kg | Medusa Type I |
| | Stone (2 % H ₂ O) | 832 kg | Sandusky Limestone |
| | Sand (6 % H ₂ O) | 625 kg | Twin Lakes |
| 10 | Water | 92 kg | |
| | Additive | ,0039 % per weight of cement | |
| | | Mix A | Mix B |
| | | Mix C | |
| 15 | <u>Mixing Time</u> | <u>Slump</u> | <u>Air</u> |
| | 4 min. | 0,114m | 4,5 % |
| | 15 min. | 0,101m | 6,5 % |
| | 30 min. | 0,076m | 6,5 % |
| 20 | 45 min. | 0,064m | 6,5 % |
| | 50 min. | 0,095m | 6,6 % |
| | (remix) ¹ | | |

25 ¹ Water was added to bring slump back to approximate original slump.

As can be seen in Table V, the additive of the invention, namely an ester-derived cocamid DEA, achieved a desirable amount of air entrainment, which proved to be relatively stable with extended mixing. This can be contrasted with Mix C which contained a Kritchevsky process-derived cocamide DEA and which produced only minimal air entrainment and which showed poor air retention. In fact, the test was stopped after 30 minutes because air dropped below the desirable minimum of 3 % air entrainment. The air content and retention values certainly seem to correlate with the foam drainage and bubble density data shown in Table I and demonstrate that ester-derived cocamide DEA is a superior air-entraining agent.

While the invention has been described with reference to certain preferred embodiments thereof, those skilled in the art will appreciate that various modifications and substitutions can be made without departing from the spirit of the invention. In particular in the context of this invention, aqueous solutions of the components described may have added thereto small amounts of compatible chelating agents for alkaline earth cations such as magnesium or calcium which normally occur in ordinary water but which would tend to precipitate surface active agents. Also, small amounts of compatible cosmetic coloring agents or biocides or the like may be added. Further, the admixture of the present invention could be used with other admixtures added for their intended purpose, e.g., the use of water-reducing admixtures to increase compressive strength or accelerating or retarding admixtures to change the rate of set of the hydraulic cement mixes. Thus it is intended that the invention will be limited only by the scope of the claims which follow.

Claims

1 - A hydraulic cement mix comprising a hydraulic cement, such as Portland cement aggregate, sufficient water to effect hydraulic setting of the cement, and an air-entraining additive consisting essentially of a coconut acid diethanolamide produced by reacting methyl ester of coconut acid with diethanolamine, said additive being in an effective amount whereby air will be entrained in said mix.

2 - A hydraulic cement mix in accordance with Claim 1, wherein said coconut fatty acid is comprised as follows :

55 Lauric Acid 46-58 %
Myristic Acid 15-23 %
Palmitic Acid 8-14 %
Stearic and Oleic Acid 7-24 %

3 - A hydraulic cement mix in accordance with Claim 1, wherein said coconut acid diethanolamide reaction product comprises :

Coconut Acid Diethanolamide 85-90 %

Coconut Acid Alkyl 0-10 %

5 Coconut Acid 0-0,5 %

Diethanol Amine 0-5 %

4 - A hydraulic cement mix in accordance with Claim 1, wherein said reaction is conducted with equal moles of coconut methyl ester and diethanolamine.

5 - A hydraulic cement mix in accordance with Claim 1, wherein said additive is in an amount of
10 between 0,001 % and 0,01 % by weight.

6 - A process for entraining air in a hydraulic cement mix, which includes hydraulic cement such as Portland cement, aggregate, and sufficient water to effect hydraulic setting of the cement, comprising the addition of an additive consisting essentially of coconut acid diethanolamide, produced by reacting methyl ester of coconut acid with diethanolamine, said additive being in an effective amount whereby air will be
15 entrained in said mix.

7 - A process for entraining air in a hydraulic cement mix in accordance with Claim 6, wherein said coconut acid is comprised as follows :

Lauric Acid 46-58 %

Myristic Acid 15-23 %

20 Palmitic Acid 8-14 %

Stearic and Oleic Acid 7-24 %

8 - A process for entraining air in a hydraulic cement mix in accordance with Claim 6, wherein said coconut acid diethanolamide reaction product comprises :

Coconut Acid Diethanolamide 85-90 %

25 Coconut Acid Alkyl 0-10 %

Coconut Acid 0-0,5 %

Diethanol Amine 0-5 %

9 - A process for entraining air in a hydraulic cement mix in accordance with Claim 6, wherein said reaction is conducted with equal moles of coconut methyl ester and diethanolamine.

30 10 - A process for entraining air in a hydraulic cement mix in accordance with Claim 6, wherein said additive is in an amount of between 0,001 % and 0,01 % by weight.

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| DOCUMENTS CONSIDERED TO BE RELEVANT | | | EP 87201266.1 |
|---|--|--|---|
| Category | Citation of document with indication, where appropriate, of relevant passages | Relevant to claim | CLASSIFICATION OF THE APPLICATION (Int. Cl.4) |
| D,X | WO - A1 - 85-01 500 (MARTIN MARIETTA CORPORATION) * Claims * -- | 1,3,5, 6,8,10 | C 04 B 24/12 C 04 B 24/08 |
| X | US - A - 3 642 506 (JOHNSON) * Claims; example IV * & CA-A-838 194 -- | 1,3,6, 8 | |
| X | US - A - 4 488 910 (NICHOLSON et al.) * Claims; tables * -- | 1,3,5, 6,8,10 | |
| Y | DR. OTTO-ALBRECHT NEUMÜLLER "Römpps Chemie-Lexikon", 8th edition, vol. 3: "H-L", 1983 FRANCKH'SCHE VERLAGSHANDLUNG, Stuttgart * Page 2164, column 1, lines 29-37 * ---- | 2,7 | |
| The present search report has been drawn up for all claims | | | TECHNICAL FIELDS SEARCHED (Int. Cl.4) C 04 B |
| Place of search VIENNA | | Date of completion of the search 07-10-1987 | Examiner BECK |
| CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document | | | |